



“Stratifiability index” – A quantitative assessment of acid stratification in flooded lead acid batteries



Dominik Schulte ^{a, b, *}, Dirk Uwe Sauer ^b, Ellen Ebner ^c, Alexander Börger ^d, Sven Gose ^e, Heinz Wenzl ^e

^a P3 energy and Storage GmbH, Am Kraftversorgungsturm 3, 52070 Aachen, Germany

^b Electrochemical Energy Conversion and Storage Systems Group¹, Institute for Power Electronics and Electrical Drives (ISEA), RWTH Aachen University, Germany

^c Volkswagen AG, Letterbox 1172, 38436 Wolfsburg, Germany

^d Volkswagen AG, Letterbox 1518, 38436 Wolfsburg, Germany

^e Electrical Energy Storage Group, Institute of Electrical Power Engineering, Clausthal University of Technology, 38678 Clausthal, Germany

H I G H L I G H T S

- Measurement of acid stratification in lead-acid batteries.
- Definition of “stratifiability index” for a quantitative assessment of acid stratification.
- Development of test procedures for building up acid stratification.
- Comparison of acid stratification in different flooded lead-acid batteries.

A R T I C L E I N F O

Article history:

Received 12 May 2014

Accepted 25 June 2014

Available online 7 July 2014

Keywords:

Flooded lead-acid

Acid stratification

Battery benchmark

Measurement of acid stratification

Lead-acid battery ageing

A B S T R A C T

A methodology is presented to quantify acid stratification in flooded lead acid batteries and compare different types of batteries regardless of their design features and size by means of the proposed “stratifiability index”. This index describes to what degree acid stratification develops in flooded lead acid batteries. Different test procedures are proposed which induce severe acid stratification within 48 h and lead to significantly different degrees of acid stratification. The test procedures are intended to assist in the development and selection of batteries which are less prone to develop severe acid stratification.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Acid stratification in lead acid batteries is caused by vertical movement of electrolyte due to differences in the specific gravity caused by inhomogeneous acid concentrations as well as by inhomogeneous charge/discharge reactions along the electrodes. Acid stratification develops in all types of lead acid batteries even in VRLA batteries where the electrolyte is immobilised in either gel or AGM [1]. In contrast to VRLA batteries, where acid stratification only develops very slowly over a period of years [1], acid stratification in flooded batteries can develop very fast and as a

consequence a permanent damage (see for instance [2]) can occur due to inhomogeneous current distribution in the vertical direction of the electrodes and, resulting in inhomogeneous states of charge in the active mass. In particular, the state of charge in the lower part of the electrodes is lower and even during standard chargings a full charging can not be achieved anymore. This finally results in large sulphate crystals and strong capacity loss due to irreversible ageing if no appropriate counter measures are applied. Removing acid stratification frequently helps to minimise the impact of acid stratification and strong charging with appropriate refreshing strategies can also prevent the sulphate crystals to grow beyond critical limits. Sauer [3], [4] and Ebner [5] have made thorough investigations of the factors which influence the development of acid stratification. Sauer has even developed a model [6] which can calculate the electrolyte density in different volume elements of a cell.

* Corresponding author. P3 energy and Storage GmbH, Am Kraftversorgungsturm 3, 52070 Aachen, Germany.

E-mail address: dominik.schulte@p3-group.com (D. Schulte).

¹ batteries@isea.rwth-aachen.de.

The speed with which acid stratification develops, the ultimate density difference between the top and the bottom of a cell, the reversible loss of capacity as a result of acid stratification and the ease with which acid stratification can be removed are design characteristics of batteries. This paper concentrates on a procedure to quantify acid stratification quickly and easily. A “stratifiability index” is proposed which describes the speed and degree with which acid stratification develops in flooded lead acid batteries after a short test procedure. Battery designers can use the test procedure to develop batteries which are less prone to acid stratification and users can use the index to select appropriate batteries if their application is likely to lead to significant acid stratification. Lifetime models for batteries have to identify use patterns which may cause acid stratification [7,8] and therefore need to be able to quantify how fast and to which extent different batteries develop acid stratification [8].

The work by Sauer [3,4] and Schulte [9] have shown that acid stratification is created often during charging of the battery – however, in some cases also discharging is important [5]. In order to create major acid stratification quickly, a deep discharge is required leading to low acid density throughout the battery cell (except the volume below the electrodes, which is, however, very small in standard SLI batteries due to envelop separators), followed by charging until the battery starts gassing significantly. Once acid stratification has developed, a subsequent discharging and charging cycle increases the density difference further. Initial experiments [10] showed that acid stratification can develop quickly within one discharge and charge cycle which is in line with the prediction of the models mentioned above.

In order to quantify acid stratification and compare different batteries and battery designs, a “stratifiability index” is required which should fulfil the following criteria:

1. easy and quick to be measured
2. applicable to all types and sizes of lead acid batteries
3. non-destructive measurement
4. meaningful values for easy interpretation

This paper describes such an index to quantify the speed and degree with which acid stratification develops. An appropriate test procedure is explained and results for different batteries are given.

Experimental and theoretical investigations as well as results from post-mortem analysis all over the world [11] show that acid stratification results in accelerated sulphation of the lower parts of the electrodes, especially in applications where small currents occur frequently. Higher acid density in the lower part and therefore a higher electrochemical potential results in inhomogeneous current distribution along the electrode. The lower part is preferably discharged (due to the higher potential) and the upper part is preferably charged (due to the lower potential). Finally, the lower part of the electrode is cycled with a local SOC which is up to 20–40% lower than the average of the electrode [12]. Therefore, the stratifiability index is an important parameter with respect to modelling and ageing of the batteries and it also helps to optimise operation strategies and selections of battery types to minimise the occurrence and the impact of acid stratification.

2. Experimental work

Two sets of experiments have been carried out in order to investigate the general occurrence of acid stratification and the possible influence of shaking (simulating driving movements) for acid stratification.

The general occurrence of acid stratification was investigated on four commercially available batteries by Gose [13] without shaking

at the laboratory of the Research Institute of Sustainable Energy (RISE) at Murdoch University, Perth Australia.

- 2 OGi 50 (50 Ah C₅, 54 Ah C₁₀, 1.24 g cm⁻³ nominal electrolyte density) from Berliner Akkumulatorenwerke GmbH, Berlin, Germany
- 47 T deep cycle (40 Ah C₅, 45 Ah C₁₀, 1.26 g cm⁻³ nominal electrolyte density) from Century Yuasa Batteries
- Faure-X 6G110 (80 Ah C₅, 110 Ah C₁₀, 1.25 g cm⁻³ nominal electrolyte density) from Exide Technologies
- 12V70 (60 Ah C₅, 70 Ah C₁₀, 1.28 g cm⁻³ nominal electrolyte density) from Akkumulatorenfabrik Moll GmbH & Co KG, Bad Staffelstein, Germany. During the manufacturing process this battery had tubes for sampling electrolyte inserted inside the pocket separator of the negative electrode in the middle between the electrodes (see Fig. 2).

These experiments are referred as “tests A” within the course of this paper.

The battery from Moll is a high performance starter battery whereas all the other batteries are industrial batteries with pasted plates for stationary, solar and other deep cycle applications.

Measurements of electrolyte density were carried out at six different heights using a specific gravity meter by Anton Parr DMA 35N which pumps approx. 3 ml of electrolyte out from the measurement point including the volume required in the sampling tube. The accuracy of the instrument is given by the manufacturer as 0.001 g cm⁻³. In order to minimise disturbance of the electrolyte as a result of removing electrolyte for measurement, each height measurement was taken in a different cell (see Fig. 1) and the electrolyte pumped out for measurement was not replaced but discarded.

Holes were drilled in the lid of the battery and a thin tube inserted into the space between the container wall and the free space between a positive and negative electrode. The measurement heights were determined in relation to the electrode length: 0% is at the bottom of the electrode, 100% at the top of the electrode and 120% in the middle of the free electrolyte above the electrodes. The other three measurements were at 18, 50 and 82% of the electrode height. The sampling tubes of the specially prepared Moll battery

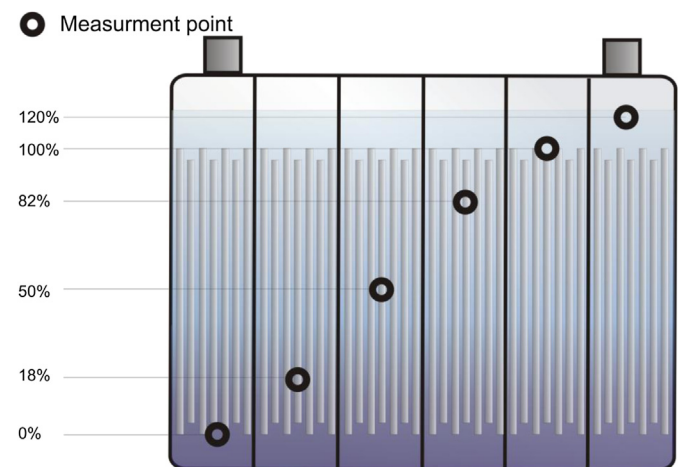


Fig. 1. Schematic diagram of a 12 V battery showing the height of the measurements which were taken in different cells. Tubes with an outer diameter of 4 mm and an inner diameter of approx. 2 mm were inserted at the edge of the cell in the space between a positive and negative electrode and the container wall. The measurement point at 120% denotes the location in the middle of the volume of the free electrolyte above the electrodes.

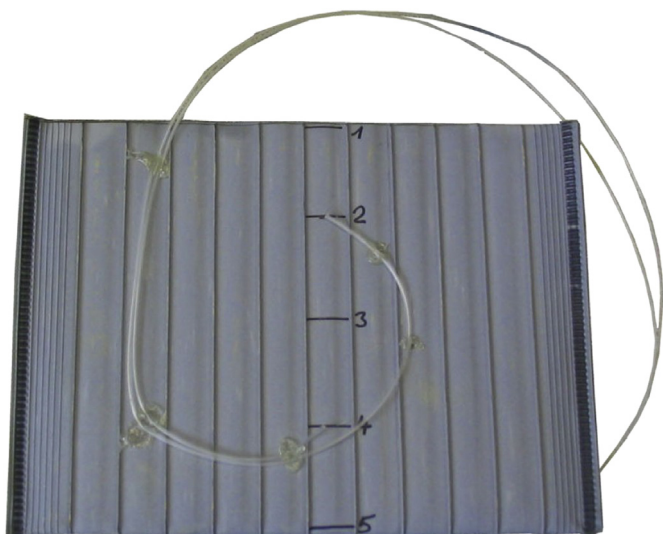


Fig. 2. Separator of the Moll 12V70 Battery showing two of the five measuring tubes, and the position of the five measuring points.

were at slightly different heights at 0, 25, 50, 75 and 100% of the electrode height and all sampling tubes were arranged inside the same pocket separator of one cell (see Fig. 2).

At the beginning of each experiment, the acid density at the various heights was measured to ensure complete removal of acid stratification from previous experiments, usually by means of prolonged charging at 2.66 V cell^{-1} in line with DIN EN 50342. The electrolyte level at the beginning of an experiment was adjusted to the maximum level indicated by the manufacturer and electrolyte was not replenished during an experiment.

The batteries were charged and discharged using test equipment from Basytec, Germany, and kept at a constant temperature of $+25^\circ\text{C}$ in a water bath throughout all the experiments. Charging or discharging was not interrupted during the acid density measurements which took approx. 5–10 min for all six measuring points.

In a second set of tests (referred as “tests B” within this paper) newly developed procedures have been investigated including shaking of two commercial SLI batteries with 72 Ah nominal capacity. Micro-reference cells acting as acid density sensors were used for measuring the acid stratification at different levels more or less continuously. This method allows *in-situ* measurements as described in detail in Ref. [9]. Each of the sensors consists initially of two isolated lead wires. After a special formation process the active surface of the tips has changed to PbO_2 , so that the sensor

is working as a lead-acid cell. Fig. 3 shows such a set of sensors. Four sensors with different lengths are combined to one set of sensors.

The sensors in combination with the related hardware measure the equilibrium voltage, which is related to acid concentration of the electrolyte in the surrounding of the tips. The acid density can be directly calculated. The acid stratification can be measured by positioning the tips of the sensors at different levels: one sensor measures the acid density in the electrolyte above the electrodes (S1), one sensor in the middle of the upper third of the electrodes (S2), one in the middle (S3) and the fourth and last one in the middle of the lower third (S4). A second set of sensors was used for the laboratory measurements due to reliability reasons. So two sensors placed in different cells measured each position simultaneously. Cell numbers three and four (the middle ones) were chosen for the measuring. Fig. 4 shows schematically the position of the sensors as well as a photo of such an equipped battery with eight sensors in the laboratory.

3. Experimental results

3.1. Tests A – 4 different batteries

To show when a battery reaches the greatest difference between the acid density at the top and bottom of the electrodes, the battery from BAE was first discharged from full charge by a constant current of $2 I_{10}$ to 1.7 V cell^{-1} and then continued to be discharged with $0.2 I_{10}$ until 1.7 V cell^{-1} was reached. Subsequently, the battery was charged with $2 I_{10}$ until 2.5 V cell^{-1} were reached and then continued to be charged for another hour at 2.5 V cell^{-1} . Figs. 5 to 8 show the results for the 2 OGi 50 battery from BAE including the times when acid density was measured. The biggest density difference is at the point when the voltage reaches 2.5 V cell^{-1} . This discharge and charge process takes approx. 39 h in all. Previous work by Carr et al. as reported in Ref. [10] had shown that the acid stratification obtained after such a single discharge and charge cycle increases only little if the process is repeated several times.

Experience with various experimental conditions has shown that acid stratification in the same battery depends mostly on the Ah removed and charged back and only little on the current amplitude during discharging. Figs. 9 and 10 show an example of this. The 2 OGi 50 battery from BAE was discharged in three steps with $2 I_{10}$, I_{10} and $0.5 I_{10}$ always until 1.7 V cell^{-1} were reached and then charged with $3 I_{10}$ until 2.5 V cell^{-1} . Despite the different current regime, the maximum acid stratification, which is achieved roughly at the point when reaching 2.5 V cell^{-1} , and the general gradient of the acid density is very similar. As can be seen, severe acid stratification can be induced after only ca. 13 h.

Based on the initial experiments, a test procedure was defined with the following objectives in mind:

- The overall test procedure should be short and a complete test (creating acid stratification and removing it) should be possible within one week. The number of acid density measurements should be as little as possible.
- The test procedure should not be so aggressive that maximum acid stratification is achieved after only one discharge and charge cycle: It was feared that a very aggressive test regime would lead to similar acid stratification after only one discharge and charge cycle and reduce possible distinctions between different batteries.
- End of discharging voltage and end of charging voltage should be within the normal limits accepted by battery manufacturers.
- Current rates normalised to the nominal capacity are used.



Fig. 3. Set of acid density sensors.

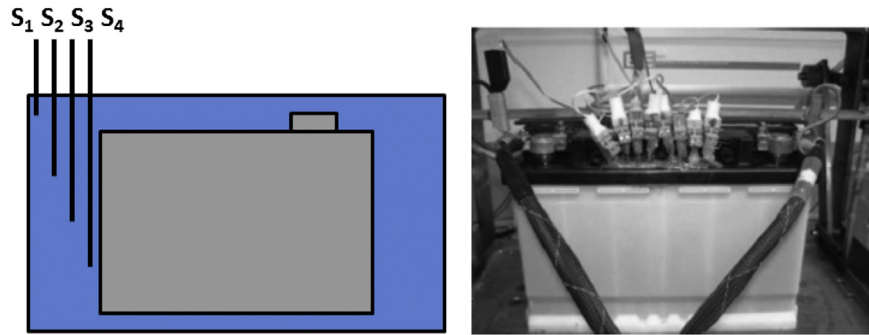


Fig. 4. Schematic overview about the experimental set-up with the four sensors (left) and a photo of the set-up in the laboratory (right).

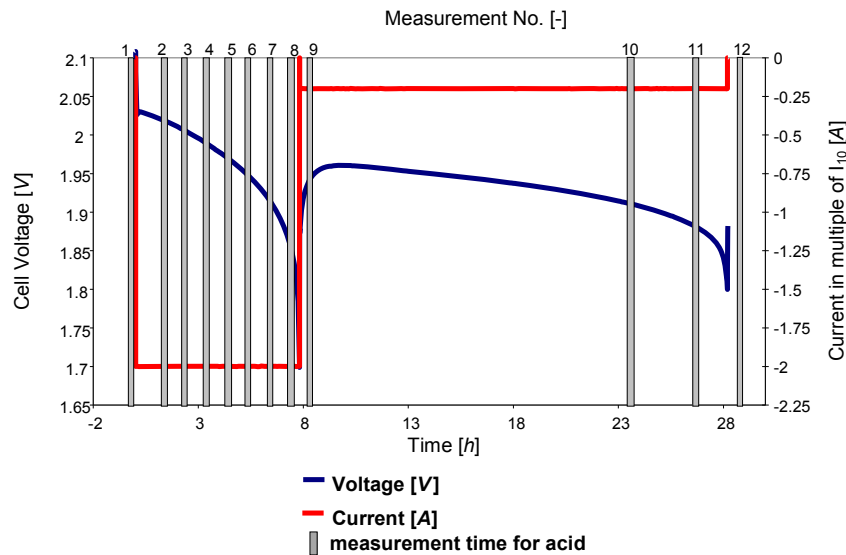


Fig. 5. Voltage and current during discharging of the 2 OGi 50 battery from BAE. The grey bars indicate the time at which the measurements were taken. The discharge of the battery was not stopped during the measurement.

The test procedure (referred to below as stratification procedure) chosen after some trials was:

1. discharging with $2 I_5$ until 1.8 V cell^{-1}
2. discharging with I_5 to 1.8 V cell^{-1}
3. discharging with $0.5 I_5$ to 1.8 V cell^{-1}

4. discharging with $0.125 I_5$ until the total discharge time was 8 h with a safety voltage limit of 1.8 V cell^{-1}

The voltage limit of the last discharging step with $0.125 I_5$ was never reached in any of the subsequent experiments. This discharging process ensures that the SOC of all batteries based on the

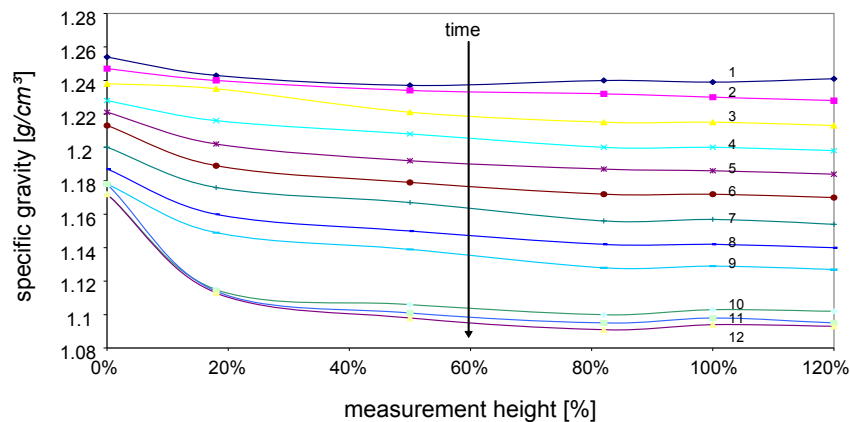


Fig. 6. Development of the acid density during discharging of the 2 OGi 50 battery from BAE. The x-axis shows the height of the electrode (0% is bottom of electrode and 100% top of the electrode). The number of the curves refers to the different measurement times shown in Fig. 5. The arrow indicates the progress of the experiment.

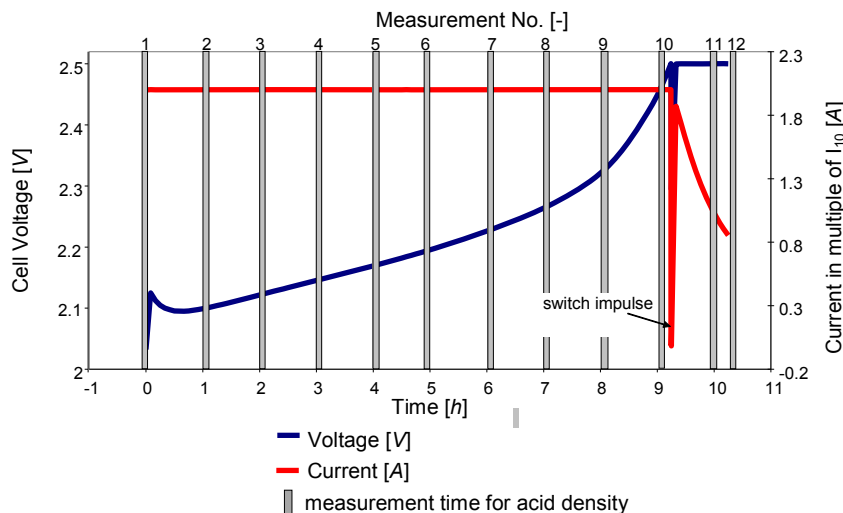


Fig. 7. Voltage and current during charging of the 2 OGi 50 battery from BAE immediately after the discharge shown in Fig. 5. The grey bars indicate the time at which the measurements were taken. The discharge of the battery was not stopped during the measurement.

actual capacity of the battery respectively the Ah removed from the battery as a percentage of the actual capacity of the battery was similar.

5. charging with $2 I_5$ until 2.4 V cell^{-1}
6. charging at 2.4 V cell^{-1} until a total time of 16 h for discharging and charging was reached.

Setting a fixed time for the end of the charging process was done so that the time for manually checking the electrolyte densities at the end of charging could be planned better.

The charging and discharging process was repeated several times. Approx. 8 h rest period were allowed after the end of every charge so that it was possible to take the density measurements always at approx. the same time of day.

Fig. 11 shows the results for the 2 OGi 50 battery for stationary applications. The results are typical for all batteries that were tested. After the first cycle, the acid density has a linear dependence on the height of the electrode which disappears after another two cycles. After three discharge and charge cycles as shown above, the electrolyte densities at the various heights did not change significantly anymore. After another two or three cycles, the difference of

acid density at the top of the electrodes and in the middle of the free electrolyte above the electrodes is nearly identical. In three of the four batteries, the difference in density increased slightly after a fourth cycle whereas with the Fauré battery, the difference decreased slightly after three discharge and charge cycles.

For the experiments it was obviously important to find a process which was capable of removing acid stratification quickly and completely. Diffusion processes reduce acid stratification only very slowly and even after 2 weeks a significant degree of acid stratification remained. Circulating the electrolyte through a pump respectively removing the electrolyte and pouring it back again immediately was found to be a very efficient method of removing acid stratification. However, removing acid stratification by overcharging is the preferred method as it does not require any auxiliary equipment or special preparation of the battery, and was therefore used in the experiments reported here. In addition, overcharging is absolutely necessary after an acid stratification occurred, because a homogenisation of the electrode is necessary. If only the electrolyte is homogenised, the main reason for accelerated ageing still remains. Fig. 8 shows that it is possible to remove acid stratification in a starter battery created by one severe discharging and charging cycle completely by a 2 h constant voltage

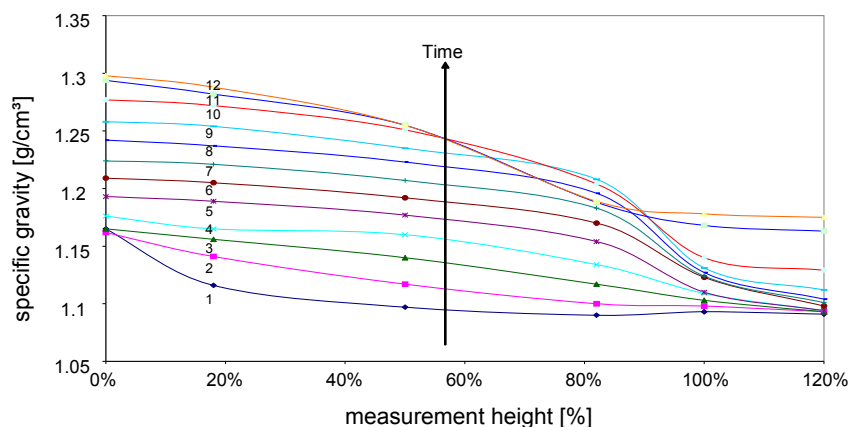


Fig. 8. Development of the acid density during charging of the 2 OGi 50 battery from BAE. The x-axis shows the height of the electrode (0% is bottom of electrode and 100% top of the electrode). The number of the curves refers to the different measurement times shown in Fig. 7. The arrow indicates the progress of the experiment.

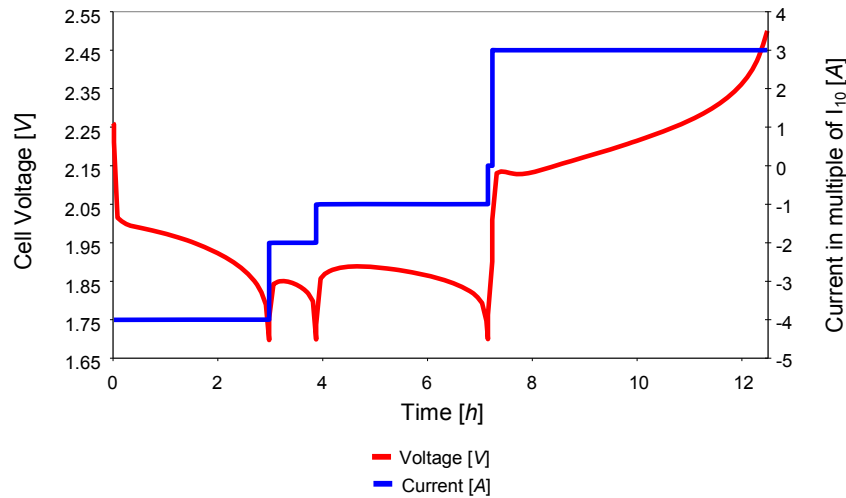


Fig. 9. Voltage and current during discharging and charging of the 2 OGi 50 battery from BAE. Acid density measurements were only taken at the end of this process.

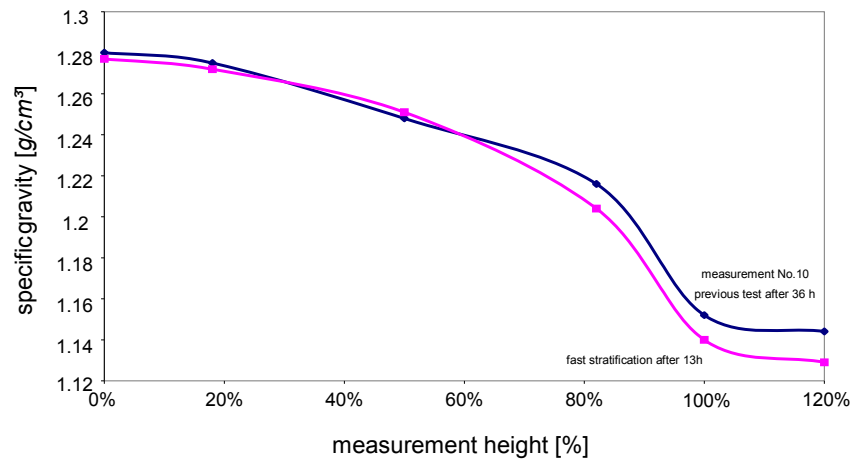


Fig. 10. Comparison of the development of the specific gravity after two different discharge and charge cycles. The purple curves shows fast acid stratification achieved after the discharging and charging regime shown in Fig. 9 (duration ca. 13 h) and the blue curve shows the maximum acid stratification achieved by means of the discharging and charging regime shown in Figs. 5 and 7 (duration 36 h). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

charge at 2.63 V cell^{-1} at the end of the charging process. However, once severe acid stratification was created by repeating the test procedure for quantifying acid stratification several times, removal of acid stratification was more difficult. For battery cells with higher electrodes removing of acid stratification by gassing is in all cases

significantly more time consuming. Fig. 12 shows that a charging regime according to DIN EN 50342 consisting of charging with $5 I_N$ until 2.66 V cell^{-1} and then continuing with 2.66 V cell^{-1} until the total charging time is 24 h did not lead to full removal of acid stratification. This is perhaps even more surprising as the batteries

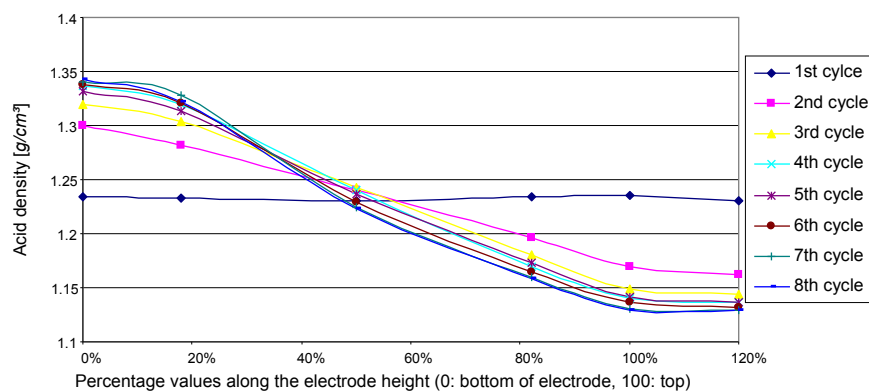


Fig. 11. Development of acid density after 8 discharge and charge cycles. Cycle 4 was started 48 h after cycle 3 and the detailed data show a slight decrease of acid stratification.

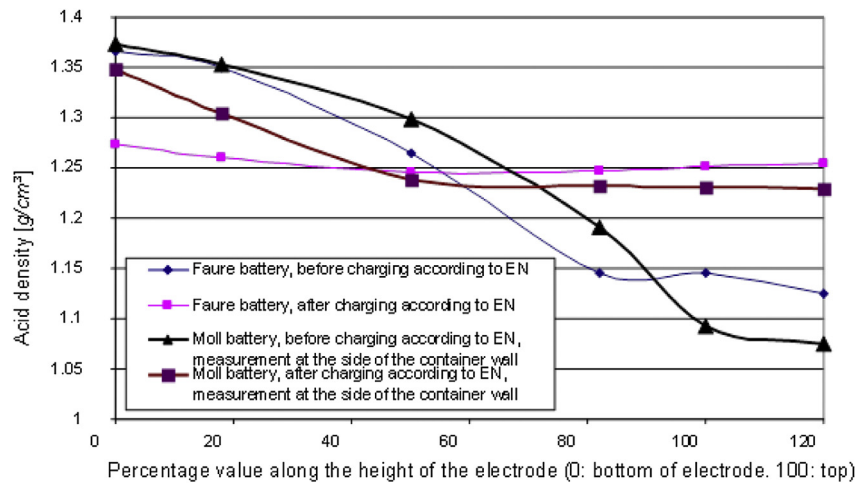


Fig. 12. Decrease of acid stratification using a charging process according to DIN EN 50342. The acid stratification before charging was created by repeating the test procedure for quantifying acid stratification several times (Moll battery: 3 times; Faure battery: 5 times).

were in a high state of charge at the beginning of the 24 h charging process according to DIN EN 50342.

3.2. Tests B – continuous measurement of acid density with shaking of batteries

Two SLI batteries (nominal capacity 72 Ah) have been aged while shaking these batteries. One of these batteries was equipped with mixing units, the other one had no mixing units as in Refs. [14] and [15]. These passive mixing units use the movements and accelerations while driving the vehicle for mixing up the electrolyte. Acid with higher density in lower regions is “pumped” into the region above the electrodes, so destratification takes place. The fully charged batteries have been discharged with $4 I_{20}$ to SOC 50%. Cycling starts with a charge ($7 I_{20}$, 2.4 V cell^{-1}) for 40 min and a discharge with $7 I_{20}$ for 30 min. These cycles have been repeated until the discharge limit of 10 V for the battery (1.67 V cell^{-1}) was reached. Acid densities have been measured during ageing by using acid density sensors. The sensors have to be recharged from time to time, so there is a dead-time for the measurement of acid density during charging (here: 2 h of charge followed by 4 h of measurement). Additionally there is an overpotential after charging as it is

well known from lead-acid batteries. A measurement of OCV and therefore of acid density is not possible in this period as well. Fig. 13 shows the acid density during the ageing in the upper part above the electrodes and in the lower region for the battery with mixing units.

There is no significant acid stratification during the test at any time. This behaviour is completely different for the battery without mixing units, as shown in Fig. 14. Acid stratification builds up very soon after starting cycling and increases during the test.

So acid stratification can be prevented by using these mixing units when shaking the batteries. The influence of the mixing units of an existing acid stratification has been also investigated in another experiment. Two batteries – one with and one without mixing units – have been equipped with acid density sensors. The cycling as in the above described experiment has been repeated, but the batteries were not shaken in the first part of the experiment. The results of the acid density measurements for both batteries are shown in Figs. 15 and 16. Acid stratification has built up during cycling in both batteries. The shaking was activated for both batteries after about 50 h of cycling. There is no significant influence of the shaking on the acid stratification in the battery without mixing units (Fig. 16). The test was finished after about 330 h,

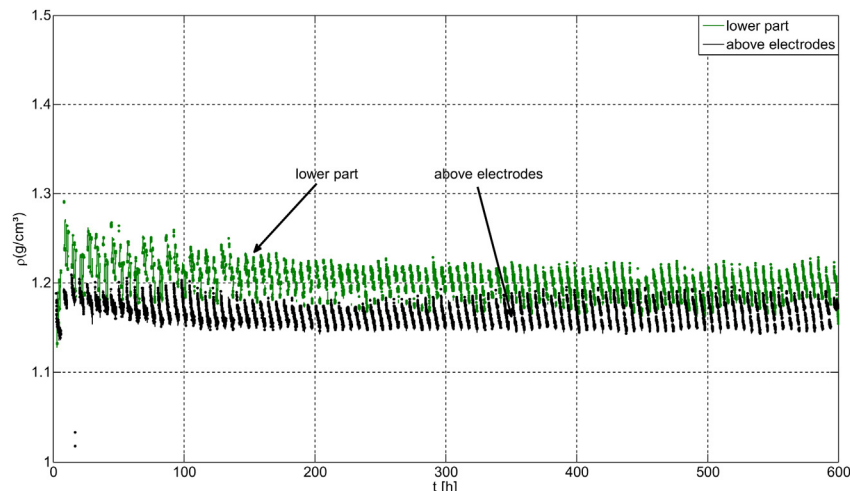


Fig. 13. Acid densities in the lower part and above the electrodes during cycling for a battery with mixing units.

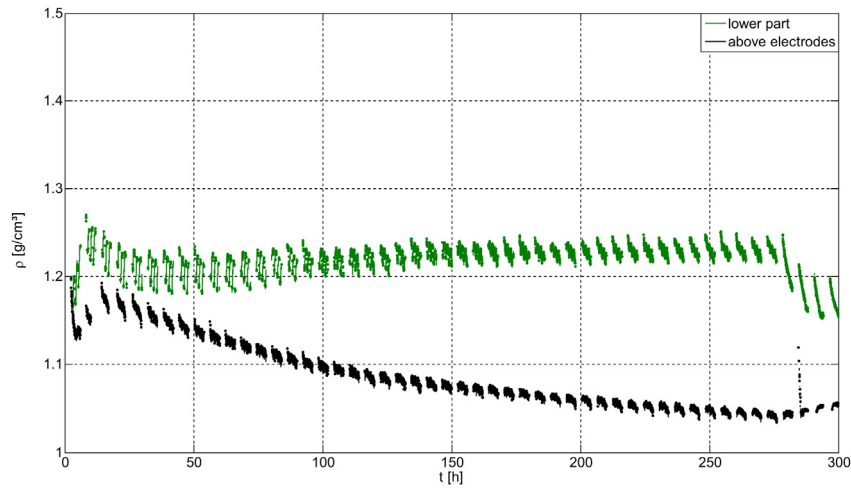


Fig. 14. Acid densities in the lower part and above the electrodes during cycling for a battery without mixing units. Cycling stops at about $t = 280$ h because voltage limit has been reached during discharging. Destratification caused by diffusion starts after cycling.

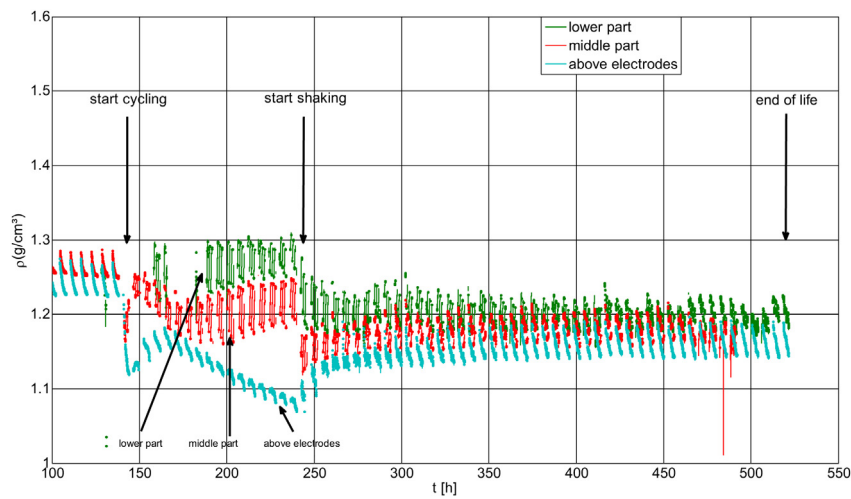


Fig. 15. Acid densities at different levels during cycling. Starting without shaking and activating shaking after about 11 h of cycling for a battery with mixing units.

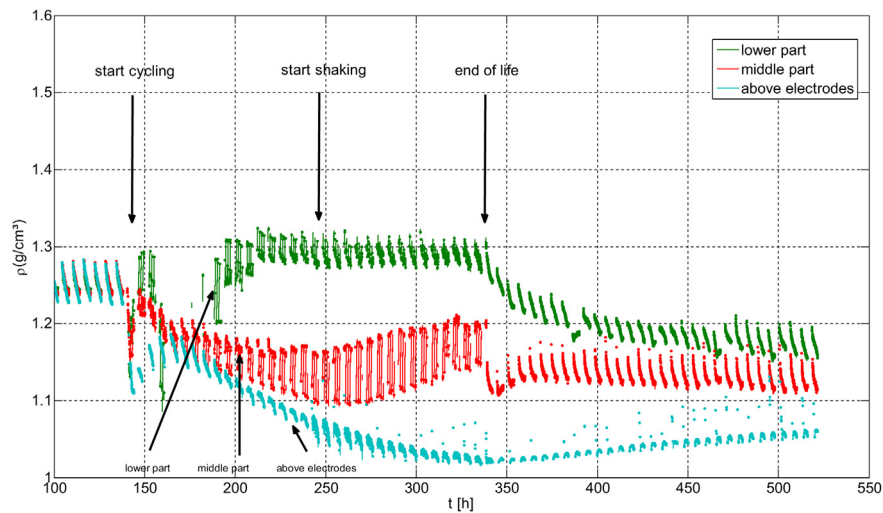


Fig. 16. Acid densities at different levels during cycling. Starting without shaking and activating shaking after about 11 h of cycling for a battery without mixing units.

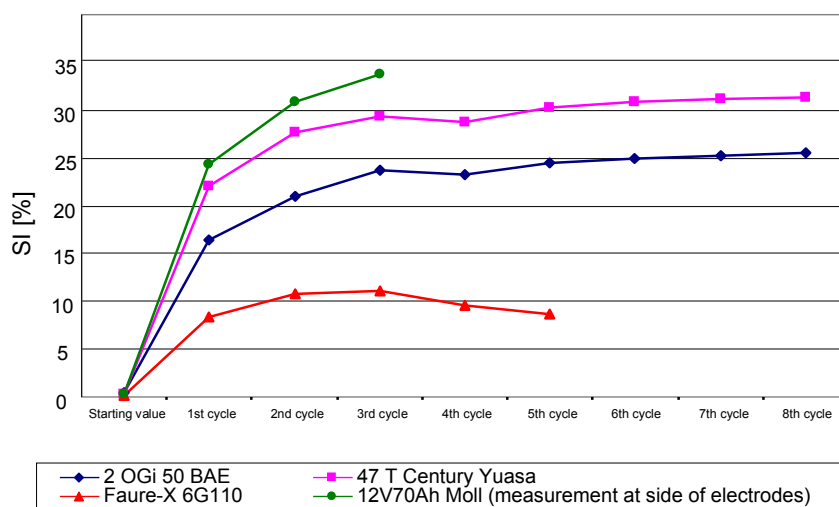


Fig. 17. Development of stratifiability index after each stratification procedure. The decrease of the stratifiability index of the BAE and Yuasa battery is due to a 48 h weekend process and indicates the effect of diffusion on the stratifiability index of a battery.

because the discharge limit was reached. The destratification caused by diffusion can be seen obviously. Fig. 15 shows the acid densities for the battery with mixing units. The stratification decreases sharply after activating the shaking (Fig. 15). Altogether, more cycles have been performed with this battery. So the mixing units in the battery are responsible for a destratification during shaking and as a result of this the lifetime can be increased significantly.

4. Discussion

Figs. 11, 15 and 16 clearly show that only two measurements are necessary to describe acid stratification quantitatively: a measurement at the bottom of the electrode and one at the top respectively in the free electrolyte above the electrode.

To quantify these results, one of the authors suggested in his student paper [13] to use an index (stratifiability index (SI)) defined as:

$$SI = \frac{\rho_{\text{lower part}} - \rho_{\text{above electrode}}}{0.84 \frac{\text{g}}{\text{cm}^3}} \cdot 100\%$$

with 0.84 g cm^{-3} being the difference in the specific gravity of concentrated sulphuric acid and water. The index is therefore zero if the electrolyte has the same density at both measuring points and has its maximum (100%), if there is 100% concentrated acid at the bottom and pure water at the top. Typical values will be in the range between 0% and about 35%.

It is worth mentioning, that the SI as defined above indicates the strength of the acid stratification in the battery cell. The SI is

therefore also an important indicator for the shift of the OCV curve in the stratified cell compared with the cell with homogenous electrolyte. However, the impact on accelerated ageing caused by acid stratification is mainly described by the difference in densities among the lower part and the upper part between the electrodes. The difference in acid concentration between the plates causes different local potentials and therefore inhomogeneous current distribution. As a result of the inhomogeneous current distribution the lower part of the electrodes falls to low states of charge and is hardly ever fully charged anymore. This finally results in strong sulphation of the lower part of the electrodes [3,5].

For the following discussion, only the value of the stratifiability index is used.

Fig. 17 shows the value of the stratifiability index for the various batteries using in all cases the stratification procedure as given above. There are clear differences between the batteries. The starter battery which was investigated has very thin plates with the negative electrode inside a pocket separator and the Fauré battery has a considerable volume of electrolyte next to the plates. As this paper aims at the development of the methodology, no further discussion is presented here concerning the possible reasons for the differences. Differences in capacity of the batteries in relation to their nominal capacity can, however, be excluded as an important factor. The percentage of the nominal capacity that was removed during the first discharge with $2 I_5$ to 1.8 V cell^{-1} is given in the following table (Table 1):

In previous experiments with the BAE battery it had been found that the capacity was considerably greater than the nominal capacity. Clearly, by comparing the differences in real capacity in relation to the nominal capacity shown in Table 1 with the SI values in Fig. 17, no correlation occurs between the capacities and the SI values. The two batteries with the highest and lowest values of the stratifiability index have very similar capacity values. Basing the currents of the stratification procedure not on the nominal capacity but on the actual capacity of the battery would remove the uncertainty. However, there is a clear advantage of using the nominal capacity of the battery for the stratification procedure. It should also be observed that the purpose of the stratifiability index is to assist designers of batteries to create batteries which are less prone to develop severe acid stratification and users to select batteries with a low tendency for acid stratification for applications with a high risk of acid stratification [7,8].

Table 1

Ah removed in the first discharging step of the stratification procedure starting with a fully charged battery with homogeneous acid density.

	Duration of discharging with $2 I_5$ [h]	Ah removed during discharging with $2 I_5$ [Ah]	Capacity C_5 [Ah]	Percentage of nominal capacity discharged during the discharge with $2 I_5$
Century	2.00	32.1	40	80.2%
OGI	3.11	62.2	50	124.3%
Faure-X	1.98	71.3	80	89.2%
Moll	2.19	52.7	60	87.9%

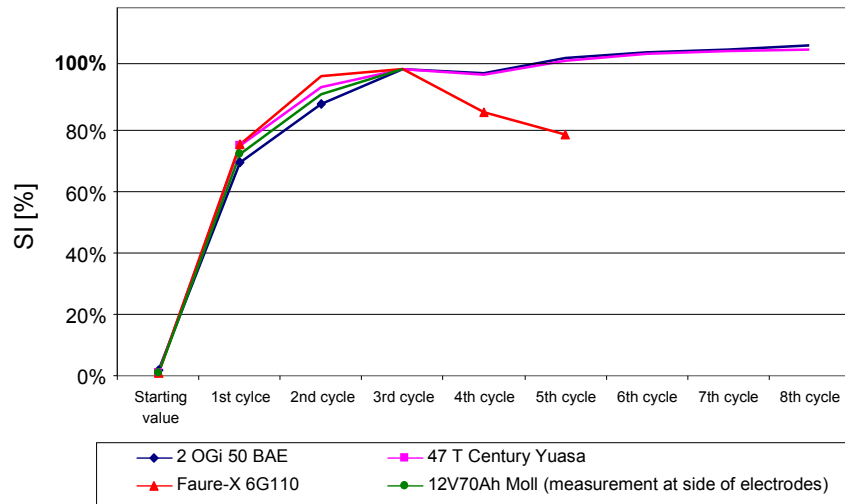


Fig. 18. Development of stratifiability index after each stratification procedure. The decrease of the stratifiability index of the BAE and Yuasa battery is due to a 48 h weekend process and indicates the effect of diffusion on the stratifiability index of a battery.

As the index reaches a stable value after three discharging and charging cycles of the stratification procedure, it is suggested to use the value at this point of the test to quantify the “stratifiability” of the battery, the property concerning the degree to which acid stratification develops. Setting the stratifiability value attained after three discharging and charging cycles to 100% (see Fig. 18) shows clearly that the rate with which this value is reached is very similar in all cases. The speed with which acid stratification develops therefore seems to be correlated with the degree of acid stratification that is attained as a stable value after three discharging and charging cycles. One value therefore is adequate to quantify the properties of a battery as regards its acid stratification properties and only two acid density measurements have to be taken. For future work it is proposed to carry out the stratification procedure three times without waiting in between the individual discharge and charge cycles, so that the total time to determine the stratifiability of the battery only takes 48 h. It is important to measure the acid density immediately after the 48 h have elapsed in order to minimise the effect of diffusion. The acid density is very similar at measuring point 100% (which is the top of the electrode) and 120% which is in the middle of the free electrolyte above the electrodes. The 120% measuring point therefore seems to be an appropriate

choice and the choice of another value, either the 100% value or the surface of the electrolyte, will not lead to different results.

The value of the stratifiability of the battery does not reflect accurately the acid density gradient. Fig. 19 shows the acid densities measured after the third stratification procedure which is used to determine the stratifiability of the battery. A lower value of the stratifiability of a battery seems to be linked with a more even acid density gradient along the electrode. When using the stratifiability of a battery for very detailed lifetime models, such a difference may be of importance.

The Moll battery which was specially prepared during production with sample tubes inside the pocket separator of one of the negative electrodes allows a comparison of the stratifiability index as measured by the two different measuring methods. For calculating the stratifiability index, the measurement at 120% was taken from a different cell. A comparison of the individual measurement results for acid density allowing for the slight difference in height at which the measurements were taken did not show significant differences. On average, the differences of acid density were 0.0092 g cm^{-3} . Only very few measurements showed a difference of more than 0.02 g cm^{-3} and there was no pattern to link these differences to a certain stage of the experiments.

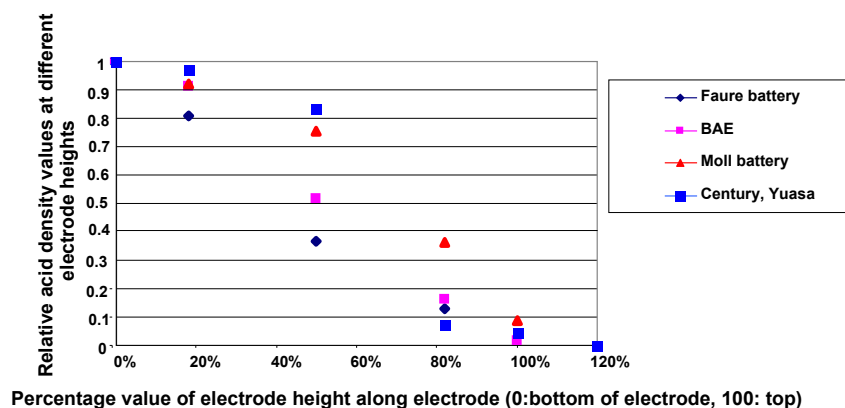


Fig. 19. Relative acid density values along the electrode height when determining the stratifiability of the battery after three stratification cycles. Acid density at the bottom of the cell (0%) has been set to 1 for each battery and acid density in the free electrolyte (120%) has been set to 0. All other measurements are relative to these two points for each battery. The relative acid density values allow a comparison of the acid gradients for different batteries.

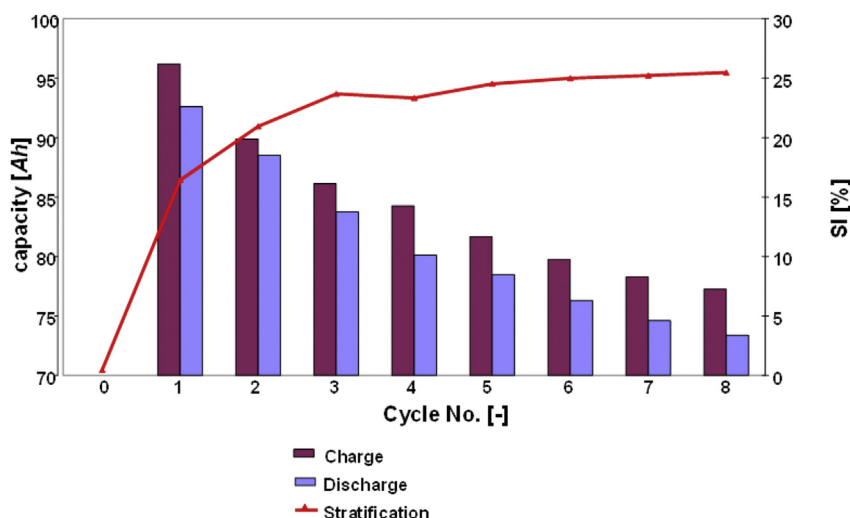


Fig. 20. Evolution of the ampere hours taken from the battery (blue bar) and charged back (purple bar) for each consecutive stratification procedure, and the stratifiability index (red curve) for the 2 OGi 50 battery from BAE. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 2

Evolution of the ampere hours taken from the battery and charged back (see Fig. 19), the charge factor and the time during the constant voltage charging phase of the stratification procedure for the 2 OGi 50 BAE battery. The total charging time in the stratification procedure is always 8 h.

Cycle no.	1	2	3	4	5	6	7	8
Discharged Ah	92.61	88.51	83.75	80.12	78.46	76.31	74.62	83.38
Charged Ah	96.20	89.88	86.13	84.25	81.67	79.75	78.29	77.27
2.4 V Charging time [h]	14.13	4.54	4.82	4.86	5.01	5.11	5.18	5.22
Charging factor	1.04	1.02	1.03	1.05	1.04	1.05	1.05	1.05

Fig. 20 shows the development of the Ah removed from the battery and the stratifiability index. There is a clear correlation between these two values which is not surprising when one considers the charge factors. If acid stratification is very severe, then the end-of-charge voltage of 2.4 V cell⁻¹ is reached more quickly and less Ah is charged back. Table 2 shows how the time at constant charging increases whereas the charge factor remains the same. Both results are typical for all the other batteries.

There are no explanations for the reduction of the stratifiability index of the Fauré battery (Fig. 18). The experiment was repeated

and showed the same result so at this point in time measurement problems can be excluded.

A surprising result of the investigations is that even an aggressive charging regime like that proposed in DIN EN 50342 is not sufficient to remove acid stratification once it has been built up to its stable value. Particularly at the bottom of the electrode, electrolyte with considerably higher density may remain (see Fig. 12).

The removal of acid stratification is linked to the gassing current – the higher the gassing current, the quicker the removal of acid stratification [9].

Fig. 21 shows the stratifiability index for the experiment with two SLI batteries and without shaking at the beginning. The SI is quite comparable for both batteries (with and without mixing units) when no shaking takes place. It increases while cycling the batteries with 17.5% DOD significantly. Shaking has been activated for both test samples at about $t \approx 240$ h. The SI for the battery with mixing units decreases sharply after activating the shaking and reaches very soon a more or less constant low level for the rest of the test ($t \approx 520$ h). The SI of the battery without mixing units is not affected by the shaking. SI increases during the whole cycling test ($t < 345$ h) and decreases after destratification caused by diffusion in the rest period.

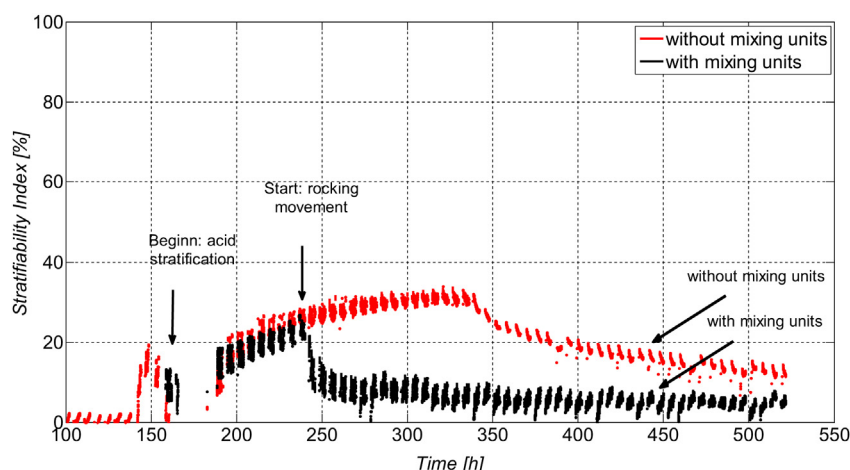


Fig. 21. Stratifiability index in dependency of cycling duration for a battery with and a battery without mixing unit during shaking.

5. Conclusions and outlook

The experiments reported here show that acid stratification can be quantified using a 48 h test procedure and taking only two electrolyte density measurements, one measurement at the bottom of the cell and the other in the free electrolyte above the electrodes. The proposed stratifiability index shows clear differences in the degree of acid stratification that develops when using the same discharging and charging procedure for different batteries. The speed with which acid stratification develops and the value of the stratifiability index after three discharging and charging cycles, the stratifiability of the battery, seem to be correlated.

The proposed method provides results within 48 h and can be applied to all types of flooded batteries. It is believed that the procedure can be used by design engineers to test the impact of certain design options on the degree of acid stratification which will develop and by users to select batteries which are not particularly prone to develop severe acid stratification if their application is likely to lead to acid stratification.

Further investigations are necessary to investigate the correlation of the stratifiability index with ageing caused by acid stratification.

Acknowledgement

The manufacture of a specially prepared battery by Moll Akkumulatorenwerke GmbH & Co. KG, Bad Staffelstein, Germany, for measuring acid density inside the sleeve of the negative electrode is gratefully acknowledged.

The authors would like to thank also Nigel Wilmot and Anna Carr from laboratory of the Research Institute of Sustainable Energy (RISE) at Murdoch University, Perth Australia for their contribution.

References

- [1] J. Garche, A. Jossen, H. Döring, *J. Power Sources* 67 (1997) 201–212.
- [2] D. Desmettre, F. Mattera, P. Malbranche, S. Métais, Publishable Report of the QUALIBAT project EU JOR3-CT97-0161, 1999.
- [3] D.U. Sauer, *J. Power Sources* 64 (1997) 181–187.
- [4] D.U. Sauer, J. Garche, *J. Power Sources* 74 (2000) 1–5.
- [5] E. Ebner, A. Börger, M. Gelbke, E. Zena, M. Wiegner, *Electrochim. Acta* 90 (2013) 219.
- [6] D.U. Sauer, *Optimierung des Einsatzes von Blei-Säure-Akkumulatoren in Photovoltaik-Hybrid-Systemen unter spezieller Berücksichtigung der Batteriealterung*, PhD thesis, University of Ulm, Germany, 2003.
- [7] V. Svoboda, H. Wenzl, R.I. Kaiser, A. Jossen, I. Baring-Gould, J. Manwell, P. Lundsager, H. Bindner, T. Cronin, P. Nørgård, A. Ruddell, A. Perujo, K. Douglas, C. Rodrigues, A. Joyce, S. Tselepis, N. van der Borg, F. Nieuwenhout, N. Wilmot, F. Mattera, et al., *Sol. Energy* 81 (2007) 1409–1425.
- [8] Vojtech Svoboda, D2.2 Categorization of Batteries in RES Applications, 2003.
- [9] D. Schulte, T. Sanders, W. Waag, J. Kowal, D.U. Sauer, E. Karden, *J. Power Sources* 221 (2013) 114–121.
- [10] Murielle le Gall, Florence Mattera, Marianne Guilmard, Marion Perrin, Anna Carr, Nigel Wilmot, D3.3: Report on Carrying Out the Proposed New Test Procedures (Practicability of Tests), 2005.
- [11] P. Ruetschi, *J. Power Sources* 127 (2004) 33–44.
- [12] D.U. Sauer, in: A. Luque, S. Hegedus (Eds.), *Handbook of Photovoltaic Engineering*, Wiley, 2003 (Chapter 18).
- [13] S. Gose, *Development of a Test Procedure for the Classification of Acid Stratification in Lead-acid Batteries*, Studienarbeit, Institute of Electrical Power Engineering, Clausthal University of Technology, 2005.
- [14] E. Ebner, M. Wark, A. Börger, *Chem. Ing. Tech.* 83 (2011) 2051.
- [15] E. Ebner, I. Metge, S.N. Keil, A. Börger, *Chem. Ing. Tech.* 85 (2013) 1294.